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(71) Applicant: SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025-3493 (US).

(72) Inventors: NARANG, Subhash, C.; 728 Garland Drive, Palo Alto, CA 94303 (US). VENTURA, Susanna, C.; 424 Becker Lane, Los Altos, CA 94022 (US). SHARMA, Sunity, K.; 2659 Alma Street, Palo Alto, CA 94306 (US). STOTTS, John, S.; 10465 Merriman Road, Cupertino, CA 95014 (US).

(74) Agents: BAROVSKY, Kenneth; Bozicevic & Reed LLP, Suite 200, 285 Hamilton Drive, Palo Alto, CA 94301 (US) et al.

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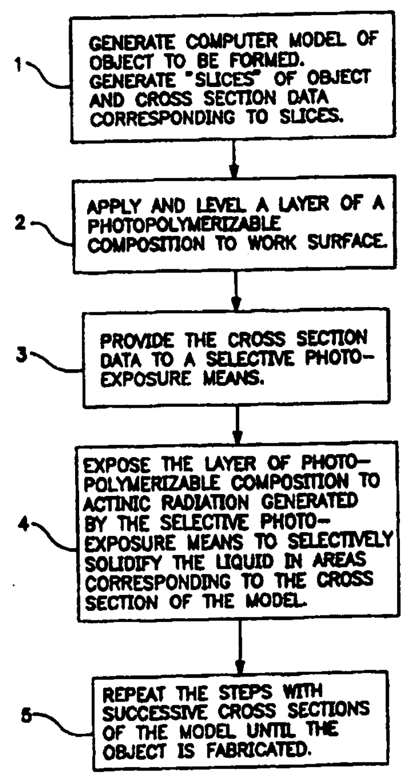
(54) Title: APPARATUS FOR AUTOMATED FABRICATION OF THREE-DIMENSIONAL OBJECTS, AND ASSOCIATED METHODS OF USE

(57) Abstract

An apparatus for fabricating three-dimensional objects using computer-controlled rapid prototyping techniques is provided. The apparatus comprises a system whereby the object is fabricated by selectively exposing a layer of a photopolymerizable composition to actinic radiation using a selective photoexposure means comprising a digital micromirror device ("DMD") for digital light processing ("DLP") projector, a liquid crystal display ("LCD") projector, an optical system for laser scanning, or a source of actinic radiation and an LCD panel displaying a computer-generated electronic mask. The photopolymerizable composition comprises a photopolymer or a high-loading ceramic or metal dispersion which, upon solidification, provides the desired structural object. Methods for forming three-dimensional objects using the apparatus are also provided.



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APPARATUS FOR AUTOMATED FABRICATION OF THREE-DIMENSIONAL OBJECTS, AND ASSOCIATED METHODS OF USE

Reference to Government Grant

This invention was made with Government support. The Government has certain rights in the invention.

Technical Field

The present invention relates generally to methods and devices for fabricating three-dimensional objects. In particular, the invention relates to a method and a device for layer-by-layer fabrication of three-dimensional objects by selective polymerization of photopolymer compositions using a selective photoexposure means, for example, a desktop digital light processing ("DLP") or liquid crystal display ("LCD") projector, an LCD panel, or an optical system for laser scanning, to effect the selective photopolymerization.

Background Art

Automated fabrication is a technology for forming three-dimensional, solid objects from raw material by automated processes. One aspect of this technology involves actinic radiation-driven solidification of specialized polymers and powders, guided by three-dimensional designs drawn on desktop computers.

Stereolithography was the first commercial "additive" process by which an object could be built by successively adding raw material in particles or layers to create a solid object of the desired shape. In this process, radiation is used to selectively solidify regions of a photo-sensitive polymer resin.

U.S. Patent Nos. 4,929,402 and 5,236,637 to Hull describe a system for generating a three-dimensional object that combines computer-generated graphics and stereolithography. The system involves "printing" thin layers of a curable material one on top of another. A programmed movable spot-beam of UV light, or other form of "synergistic stimulation" such as electron beams, visible light or invisible light, is

moved across the surface of each layer to form a solid cross-section of the object at the surface of the layer.

The introduction of stereolithography stimulated the development of a number of additive fabrication processes. Current additive processes also use a layering method to build the desired object in horizontal layers. The layers are typically about 0.1 to 0.25 mm thick, so the process requires about 40 to 100 layers per vertical centimeter of the object.

One such process is "selective photocuring." Selective photocuring processes, which include the original stereolithographic technique, use a liquid photopolymer that has the property of solidifying under the influence of light of a particular wavelength. Current photocuring-based fabricators work by laying down a thin layer of photopolymer and shining the proper wavelength of light on it in a pattern that describes the two-dimensional shape of a cross section of the object to be built. The pattern may be expressed by scanning a laser beam over the layer, turning it on and off as needed to solidify predetermined sections of the layer. Alternatively, the layer may be expressed by shining a lamp through a mask that lets light through where the layer should be solid and blocks light from those areas that should not be solid. Once a single cross section is built in this manner, a new layer of photopolymer is applied and the process repeated to form the whole object.

Many current systems use a vat of liquid photopolymer in which to build the object. Rather than penetrating deeply into the photopolymer, the light induces solidification only near the surface. A platform is placed under the area where the object is to be fabricated and, as each layer is formed at the surface, the platform and the previously formed layer recede into the vat, typically by about 0.1 mm, to allow a fresh layer of liquid polymer to form over the top of the previous layer. This can be also accomplished by starting with an empty vat and feeding in enough photopolymer for one layer's thickness after each layer is built.

Three-dimensi nal laser-curing fabricators are known in the art. Systems that incorporate this technology are commercially available from, for example, 3D Systems (Valencia, CA), CMET (Tokyo), S ny (Tokyo), EOS GmbH (Munich), and

Teijin Seiki (Tokyo). A fabricator that uses masked-lamp curing is available from Cubital (Raanana, Israel).

The masked-lamp photopolymer fabricator available from Cubital generates a mask by ionographic printing, a process similar to xerography. The mask image is created by attracting particles of toner to the appropriate regions of a glass plate by static electricity. After the mask is used, the powder is wiped off and recycled for use in the next mask. The process includes spreading a layer of resin onto a surface, exposing the layer to curing ultraviolet light through the mask, and removing the uncured resin by vacuum suction. Molten wax is then spread over the cured layer to fill the voids left by the removed resin and provide support for the object as fabrication proceeds.

Such rapid prototyping processes are presently being applied to the fabrication of nonstructural materials by means of computer-aided design/computer-aided manufacturing ("CAD/CAM") technology, wherein computer files descriptive of the object to be fabricated are used to create parts from materials such as UV-curable polymers. The components fabricated in this fashion are generally considered nonfunctional, and their main application is for iterative design evaluation.

There is an increasing demand, however, to extend rapid prototyping technology to the fabrication of functional components with engineering properties and dimensional tolerances comparable to those of conventionally produced components. The development of advanced solid freeform fabrication ("SFF") manufacturing technology allows the fabrication of functional prototypes from advanced ceramic, metallic, and multiphase materials for structural and electronic applications.

The present invention is directed to an apparatus and method for preparing functional prototypes using layer-by-layer photofabrication. The system disclosed herein produces functional prototypes in a rapid and cost-effective manner.

<u>Overview of Related Art</u>

The following patents and publications relate to one or more aspects of the present invention, and reference may be made thereto for background information not

explicitly included herein concerning processes of fabricating three-dimensional objects, photopolymers, and the like.

U.S. Patent No. 4,906,424 to Hughes et al. describes a composition containing 50 vol.% to 87 vol.% ceramic powder or metal powder dispersed in a polymerizable monomer and, optionally, a plasticizer and a surfactant.

U.S. Patent No. 5,496,892 to Quadir et al. describes a composition containing 40 vol.% to 70 vol.% sinterable ceramic and/or metal particles, a photocurable monomer, a photoinitiator, a dispersant, and a coupling agent.

U.S. Patent No. 4,961,154 to Pomerantz et al. describes a apparatus for preparing a three-dimensional model of an object. The apparatus includes a optical apparatus for irradiating a layer of solidifiable liquid, e.g., a conventional slide projector, a apparatus for accurate positioning and registration of a plurality of pattern masks, a means for generating the pattern masks by a photographic technique, such as photographic film, or by an electrophotographic technique, e.g., by depositing a toner on a glass plate in a desired pattern.

U.S. Patent No. 5,263,130 to Pomerantz et al. describes a system for providing a three-dimensional physical model by sequentially irradiating layers of a solidifiable liquid using masks to solidify the appropriate portion of the model and then removing the non-solidified material. The mask may be a graphic mask, e.g, a transparent material on which a mask is formed, an erasable mask written directly onto the surface of the solidifiable liquid, or an electronic line mask, e.g., a linear liquid crystal array, that, along with the light source, is translated across the surface of the liquid.

U.S. Patent No. 5,287,435 to Cohen et al. describes an apparatus and a method for producing a three-dimensional object by depositing, layer upon layer, a photopolymer material, curing each layer by exposing the material through a mask defining a layered cross section of the object. The mask is an ionographic image developed by depositing toner onto ionized portions of a transparent substrate.

U.S. Patent No. 5,398,193 to deAngelis describes a Rapid Prototyping System that involves providing a three-dimensional computer model representation of the part to be fabricated and preparing slices of the model that correspond to successive layers of the model from a material that is processable by heating, chemical treatment or

energy treatment. The processable material include metals, ceramics, and thermoforming and thermosetting plastics. The system optionally includes the formation and use of a mask-forming subsystem that produces masks cut into a continuous film or a set of individual mask sheets.

Disclosure of the Invention

Accordingly, it is a primary object of the invention to address the aforementioned need in the art by providing a device for the automated fabrication of a three-dimensional object.

It is another object of the invention to provide a device for fabricating a three-dimensional object using a photopolymerizable composition that is selectively solidified by exposure to actinic radiation generated by selective photoexposure means.

It is yet another object of the invention to provide a method for fabricating a three-dimensional object using such device.

Additional objects, advantages and novel features of the invention will be set forth in part in the description that follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

In one aspect of the invention, an apparatus is provided for automated layer-by-layer fabrication of a three-dimensional object from a computer model of the object. The apparatus comprises: a work surface on which the three-dimensional object is fabricated; a means for depositing a predetermined quantity of a photopolymerizable composition onto the work surface; a means for leveling the deposited composition to a layer having a predetermined thickness; selective photoexposure means for selectively exposing the layer to actinic radiation to cure those areas of the layer that correspond to a cross section of the object; a CAD/CAM system comprising a means for producing a three-dimensional computer model representation of the object, a means for slicing the representation into a plurality of successive layers having predetermined thickness, a means for producing cross section

data of the layers of the object, and a means for providing the cross section data layerwise to the selective photoexposure means.

In a further aspect of the invention, a method for fabricating a functional three-dimensional object is provided that comprises: applying a first layer of a photocurable composition on a work surface, wherein the layer is sufficiently thin to permit photopolymerization substantially the entirety thereof; exposing the first layer to actinic radiation using computer-controlled selective photoexposure means for a period of time sufficient to photopolymerize the area of the layer which is exposed to the radiation; repeating the application and exposure steps; and applying additional layers of the composition to the previously photopolymerized layer, wherein with each additional layer the computer-controlled selective photoexposure means is changed to correspond to a cross section of the object immediately adjacent to the cross section of the previously prepared layer, until the object has been fabricated.

Brief Description of the Drawings

FIG. 1 is a block diagram of a method for fabricating a three-dimensional object according to the present invention.

FIG. 2 is an illustration of a system by which a three-dimensional object can be fabricated in accordance with one embodiment of the invention.

FIG. 3 is an illustration of a system by which a three-dimensional object can be fabricated in accordance with another embodiment of the invention.

Modes for Carrying Out the Invention

The practice of the present invention will employ, unless otherwise indicated, conventional techniques of photochemistry, ceramic chemistry, polymer chemistry, and rapid prototyping and manufacturing that are within the skill of the art. Such techniques are explained fully in the literature. *See*, e.g., Kirk-Othmer's Encyclopedia of Chemical Technology, Burns Automated Fabrication (PTR Prentice Hall, Englewood Cliffs, NJ (1993)), and Jacobs, Rapid Prototyping and Manufacturing: Fundamentals of Stereolithography (Society of Manufacturing Engineers, Dearborn, MI (1992)).

Definitions:

Before describing the present invention in detail, it is to be understood that this invention is not limited to a particular photopolymerizable composition, methods of their preparation, solvents, or the like, as such may vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

It must be noted that, as used in this specification and the appended claims, the singular forms "a," "an" and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to "a ceramic powder" includes mixtures of such powders, reference to "a polymerizable monomer" includes more than one such monomer, reference to "a layer" includes more than one such layer, and the like.

In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

The term "fabrication" is intended to mean the generation of a solid three-dimensional object, with some specific desired shape and physical properties.

"Visible light" is electromagnetic radiation with wavelengths ranging from 4×10^3 Å to about 7.7×10^3 Å. "Near infrared light" or "near IR light" is electromagnetic radiation with wavelengths ranging from 7.5×10^3 Å to about 30×10^3 Å. "Actinic radiation" is radiation capable of initiating photochemical reactions.

"Optional" or "optionally" means that the subsequently described circumstance may or may not occur, and that the description includes instances in which said circumstance occurs and instances in which it does not. For example, the phrase "optionally including a ceramic powder" means that a ceramic powder may or may not be present and that the description includes both the instance when the ceramic powder is present and the instance when the ceramic powder is not present.

The invention, together with additional features and advantages thereof, may be best understood by reference to the following description taken in connection with the illustrative drawings.

With reference to FIG. 1, a flow chart is provided illustrating the steps us in conjunction with the invention. Basically, a three-dimensional complex-shape object

is formed by selective photoexposure of the layers, one at a time, using a computer-controlled selective photoexposure means to project an image of a layer onto the surface of the photopolymerizable composition. In step 1, a computer representation of the object to be formed is generated using a CAD/CAM software system; the CAD/CAM software generates STL files. The STL files are then converted into "slice" data. In other words, the computer representation generated by the CAD/CAM software is "sliced" into layers that correspond to each of the layers that, in aggregate, will form the object upon completion of the fabrication process. Each "slice" of the object is converted into data corresponding to a two-dimensional cross section of the layer.

In step 2, a layer of a photopolymerizable composition is applied to a movable work surface on which the object is to be formed. The composition is applied and leveled to a desired thickness to correspond to the thickness of the "slice" generated by the computer.

In step 3, the data corresponding to the two-dimensional cross section of the layer is fed to a selective photoexposure means for selectively exposing the photopolymerizable composition to actinic radiation. In one embodiment, the selective photoexposure means comprises a DLP or LCD desktop projector capable of receiving the slice data generated by the computer and projecting the layer image onto the composition. Alternatively, the selective photoexposure means comprises a source of actinic radiation and a computer-generated mask displayed on an LCD panel that allows actinic radiation to pass therethrough in areas corresponding to areas of the photopolymerizable composition to be solidified. The mask blocks the passage of radiation from areas of the layer not to be solidified. In a different embodiment, the selective photoexposure means comprises scanning layer optics.

Upon exposure to such radiation, as in step 4, the photopolymerizable composition is selectively polymerized to form a cross section of the layer of the object corresponding to the computer-generated section. After the formation of a layer, the process is repeated as outlined in step 5 to form additional layers over each previously formed layer until the object is fabricated.

FIG. 2 illustrates one embodiment of an apparatus suitable for implementing the method illustrated and described in the flow chart of FIG. 1, and, is shown generally at **20**. Device **20** comprises a work surface **22** having a build table **24** with a superior face **26** that can be displaced vertically by way of elevator means **28**, e.g., a stepper motor, or the like. A photopolymerizable composition **30** is dispensed onto work surface **22** from, for example, pressurized tank **32**, through valve **33** and then through suitable ports **34** in the work surface. Alternatively, the composition **30** may be routed through valve **33** to conduit **36** and directly to work surface **22**. The photopolymerizable composition **30** is applied over the work surface to a predetermined thickness by leveling means **38**, e.g., a doctor blade, to form layer **40** on build table **24**. A typical layer thickness ranges between 1 mil to 25 mil, preferably between 1 mil to 10 mil. Excess material is optionally removed by action of recovery means **42**, e.g., a "squeegee," through drain **44** into recovery vat **46**. The leveling means is then raised and vertical positioning means **48**, e.g., a pneumatic cylinder, lowers selective photoexposure means **50** held in frame **52**. The layer of photopolymerizable composition **30** is selectively exposed to actinic radiation by activating selective photoexposure means **50**. Any uncured material is removed, e.g., by aspiration. A solvent, e.g., hexane, acetone, or the like, may be used as an aid to dislodge the uncured material.

In one embodiment, selective photoexposure means **50** comprises a digital micromirror device ("DMD") for DLP projector or an LCD projector. Such projectors are designed to interface with CAD/CAM and STL slice conversion software. The slice information is converted to a cross section image of the layer and light is projected corresponding to those areas of the layer to be photopolymerized. The image projected by the DLP or LCD projector is controlled by computer system **54**. DMD for DLP projectors may be obtained, for example, from Proxima (Desktop Projector Model 4100) or InFocus Systems (Lite Pro 620). LCD projectors may be obtained from Proxima (Desktop Projector Model 240) or InFocus Systems (Lite Pro 210).

In another embodiment, the selective photoexposure means comprises a source of actinic radiation, an LCD panel that serves as an electronic mask, and optical

elements as needed to collimate, focus, filter, or otherwise process the radiation that passes through the mask as required. Those skilled in the art will recognize that the optical elements may include various lenses, mirrors, filters, and the like, depending on the source of radiation and the nature of the photopolymerizable composition. The data corresponding to the two-dimensional cross section of the layer is fed to the LCD panel to create an electronic mask, through which actinic radiation passes to solidify selected areas of the photopolymerizable composition as discussed above. The ability of the LCD panel to pass or block the passage of the radiation is controlled by computer system **54**. The LCD panel may be one having an active or a passive matrix screen. LCD panels that may be used with the layer-by-layer photofabrication system disclosed herein are commercially available from, e.g., nView Model Z310 (nView, Newport News, VA).

In a third embodiment, illustrated in FIG. 3, selective exposure means **50'** comprises an optical system for laser scanning. A description of an exemplary optical system for laser scanning may be found in Fisli (1983) *Proc. SPIE Int'l Soc. Optical Eng.* 390:45-48. Preferably, system **50'** is affixed to leveling means **38** in a manner such that as the photopolymerizable composition is applied over the work surface to a predetermined thickness by the leveling means, the optical system is translated over the surface of the layer of photopolymerizable composition. The optical system for laser scanning **50'** is loaded with an image of a cross section of the layer to be fabricated from computer **54**. The image stored in the laser printer optics system is fed to the laser which serves to selectively expose the composition to radiation, and thereby solidifies those areas of the composition corresponding to the cross section of the object to be formed. The laser is preferably a solid-state diode laser which can be used to generate actinic radiation in the near infrared spectrum or, with the use of a frequency doubler, in the visible spectrum. Optical systems for laser scanning are available from Xerox Corp. (Palo Alto, CA). Solid-state lasers that emit in the visible or near IR spectral ranges are available from SDL®, Inc. (San Jose, CA) or Uniphase (San Jose, CA).

A suitable source of actinic radiation is a visible light source or a near infrared light source. The visible light source may be a tungsten-halogen lamp, a xenon arc

lamp, e.g., Oriel 1000 Xenon arc lamp, or a visible solid-state laser. Near infrared light sources include solid-state diode lasers, quartz tungsten-halogen lamps, and the like.

Computer system **54** is used to generate a three-dimensional model of the object to be fabricated. The computer-generated model may be constructed on the computer itself, using CAD/CAM software. In the alternative, the model may be generated from data scanned into the computer from a prototype or from a drawing. The computer is thus used to provide slice information about the various layers of the object and to provide cross section data for each layer that is fed to selective photoexposure means **50**. The computer-generated slice information may be provided to selective photoexposure means **50** at any time prior to exposure of the photopolymer to the radiation. Guidance for the selection of appropriate CAD/CAM and slice conversion software may be found in Jacobs (1992), *supra*, chapters 5 and 6, and Burns (1993), *supra*, chapter 6.

Computer system **54** may be any system that is capable of modeling the object to be fabricated, slicing the model into layers having predetermined thickness and providing two-dimensional cross section data about the layer to selective exposure means **50** or the optical system for laser scanning. Examples of such systems have been described in U.S. Patent No. 4,961,154, *supra*, and U.S. Patent No. 5,182,715 to Vorgitch et al. CAD/CAM software is available from a number of vendors including, e.g., EDS-Unigraphics (Troy, MI), Structural Dynamic Research Corporation (Milford, OH), Hewlett-Packard Mechanical Division (Ft. Collins, CO), Autodesk (Sausalito, CA). STL conversion software for rapid prototyping is available from vendors such as Brock Rooney and Associates (Birmingham MI), Imageware (Ann Arbor, MI), Solid Concepts, Inc. (Valencia, CA), POGO International, Inc. (College Station, TX), and the like.

Computer system **54** may perform a variety of functions in addition to generating the three-dimensional model of the object to be fabricated, the slice information about the layers of the object, and the cross section data for each layer, from which the mask is generated. Computer system **54** may be used to control the operation f elevator means **28**, valve **33**, vertical positioning means **48**, and the like.

When exposure of a layer is complete, selective photoexposure means **50** is returned to an elevated position to allow the application of a new layer of photopolymerizable composition to enable communication of data to the selective photoexposure means for generation of the cross section image of the successive layer. A three-dimensional object is accordingly produced by the step-wise buildup of layers, such as ***40a***, ***40b***, and ***40c***, on build table **24**.

The build table **24** is used to support and hold the object during fabrication, and to move the object vertically as needed. Typically, after a layer is formed thereon, the build table is moved down so a fresh layer of photopolymerizable composition may be applied over the just-formed layer. Elevator means **28** should be capable of programmed movement at an appropriate speed with appropriate precision. The elevator means movement mechanism may be mechanical, pneumatic, hydraulic, or electric, and may include optical feedback to control its position relative to the work surface.

The photopolymerizable composition may include any uncured liquid, semi-solid or solid that can be cured by actinic radiation, e.g., by visible light, near infrared light, or the like. Examples of such curable liquids, semi-solids and solids are disclosed in <u>UV Curing: Science and Technology</u>, Pappas, ed., Technology Marketing Corp. (Norwalk, CT), and Roffey, <u>Photopolymerization of Surface Coatings</u>, J. Wiley & Sons (Chichester). Photopolymerizable resins are commercially available from, e.g., Applied Polymer Systems, Inc. (Schaumberg, IL), Ciba Geigy Corp. (Los Angeles, CA), UCB Chemical Corp., Inc. (Smyrna, GA), E.I. Du Pont de Nemours & Co. (Wilmington, DE) and Sartomer (Exton, PA).

The polymerizable component of the dispersion is a monomer, mixture of monomers, oligomers, mixtures of oligomers, or mixture of oligomers and monomers, which can be polymerized and solidified by exposure to actinic radiation such as near infrared or visible light. Suitable photoactive monomers include acrylates, including mono-, di- and tri-acrylates, and mixtures thereof, methacrylates (*see*, Tu, *in* <u>UV Curing Science and Technology</u>, Pappas, ed., *supra*, Chapter 5), epoxides, or epoxide-acrylate formulations, and other visible or near infrared light curable monomers. Examples include 2-hydroxyethylacrylate, hexanedioldiacrylate, triethyleneglycol-

diacrylate ("TEGDA"), diethyleneglycoldiacrylate, tetraethyleneglycoldiacrylate, tri-methylolacrylate, and the like.

In one embodiment, a solid or semi-solid photopolymerizable composition may be formulated from a photopolymerizable monomer, or oligomer, or both, mixed with a polymer that is optionally functionalized to have moieties with which the monomer or oligomer may react. Alternatively, the monomer, oligomer, or both may be mixed with a wax. Preferably, the monomer is an epoxide, e.g. Uvecure® 1500 (UCB Chemical Corp.), 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (Aldrich), or 1,4-butanedioldiglycidylether (Aldrich), or an epoxyacrylate such as Ebecryl® 3200 (UCB Chemical Corp). More preferably, the monomer is an epoxide-acrylate blend. The oligomer may be a polyesteracrylate oligomer, such as, Ubecryl® 438, Ubecryl® 584, or Ubecryl® 2047. Examples of waxes that may be incorporated into the photopolymerizable composition include paraffin waxes, microcrystalline waxes, carnauba wax, mineral wax, synthetic waxes, such as polyethylene waxes, and the like (*see*, Encyclopedia of Polymer Science and Engineering, 2nd edn., vol. 17, pages 784-795).

A semi-solid or solid photopolymer composition is dispensed onto the work table as a hot liquid. As the liquid cools it solidifies. The solidified composition is photopolymerized by exposure to an appropriate wavelength of actinic radiation. When a solid or semi-solid photopolymerizable composition is used, additional support components or structures may or may not be designed into the object.

The photopolymerizable composition may also include a plasticizing solvent. Solvents having plasticizing properties include dibutylphthalate ("DBP"), benzylbutylphthalate, other phthalates, linear or cyclic carbonates such as propylene carbonate and ethylene carbonate, ketones such as cyclohexanone, methylethylketone, and higher homologs, ethers, and the like. Additional optional components that can be included in the photopolymerizable composition may be found in U.S. Patent No. 4,906,424 to Hughes et al.

Optionally, a light-sensitive additive is incorporated into the photopolymerizable composition to reduce the energy necessary to effect photo-polymerization. Visible light photoinitiators are generally multicomponent systems

including, e.g., a xanthene dye, a first coinitiator such as an iodonium salt, and a second coinitiator. Suitable visible-near IR photoinitiators are described in U.S. Patent Nos. 5,451,343 to Neckers et al., 5,395,862 to Neckers et al., 4,952,480 to Yamaguchi et al, and 4,772,530 to Gottschalk et al., De Raaff et al. (1996) *RADTECH Conference Proceedings*, Chatterjee et al. (1988) *J. Am. Chem. Soc.* 110:2326-2328, Bi et al. (1994) *Macromolecules* 27:3683-3693, and include 3,3'-diethylthiatricarbocyanine iodide, 3,3'-diethylthiadicarbocyanine iodide, 3,3'-diethyloxadicarbocyanine iodide, 3,3'-dimethyloxatricarbocyanine iodide, 1,3,3,1',3',3'-hexamethylindodicarbocyanine iodide, and 1,1'-diethyl-2,2'-quinodicarbocyanine iodide, all of which are commercially available (e.g., from Dojindo Laboratories, Japan, or from Spectra Group Limited, Inc., Maumee, OH).

As each successive layer of the object is fabricated from a liquid photopolymerizable composition, it may be necessary to provide structural support for elements of the object. Means for providing such support are well known in the art and may be incorporated into the object as it is being fabricated. Such elements may be removed when fabrication of the object is complete. For examples of such support structures, see, Burns, *supra*, chapter 6, and Jacobs, *supra*, chapter 6. Any of the means described in these references, or any other means of providing support known to those skilled in the art may be used. When a solid or semi-solid photopolymerizable material, such as a composition containing a wax, is used to fabricate the object, additional support structural elements may or may not be designed into the object.

In order to produce a structural and/or functional material using the automated additive method disclosed herein, a high ceramic- or metallic-loading dispersion comprising a polymerizable monomer or oligomer with low viscosity is used. The dispersion is a combination of components: a solvent having plasticizing properties, such as phthalates, cyclic or linear carbonates, ketones, ethers, and the like; a surfactant or dispersant, such as Hypermer®, Triton® X-100, Brij®, and the like; polymerizable monomers; and, optionally, a wax, a ceramic material, a metallic material, or a mixture thereof.

The composition is prepared by dispersing a ceramic powder, a metallic powder, or both, into a photopolymerizable monomer, mixture of monomers, oligomer, or mixture of monomer and oligomer. The ceramic or metallic powder will comprise at least about 50 wt.% to about 90 wt.% of the composition. The ceramic and metal powders are preferably in a finely divided form, preferably having diameters in the range of from about 0.1 μm to about 50 μm, preferably about 0.1 μm to about 1.0 μm. The powder should be selected so that close packing of the powder particles may be achieved in the dispersion.

Any ceramic or metallic powder that can be formed into finely divided particles can be used in the photopolymerizable composition. Examples of suitable ceramic powders include silica, silicon nitride, silicon carbide, boron carbide, titanium carbide, titanium nitride, tungsten carbide, molybdenum oxide, alumina, zirconia, silicon, ferrite, and mixtures thereof. Examples of suitable metallic powders include free metals such as aluminum, copper, nickel, iron, magnesium, silicon, titanium, tungsten, mixtures thereof, alloys thereof, such as stainless steel, nickel aluminum, titanium aluminum, and the like, mixtures of alloys thereof, and mixtures of metals and metal alloys.

Suitable software is used to provide data to the selective photoexposure means for generation of the successive layer cross section images. The selective photoexposure means is linked to a CAD/CAM system and a slice conversion system that are together capable of producing a three-dimensional computer model representation of the object, slicing the representation into a plurality of successive layers having predetermined thickness, producing cross section data of the layers of the object, and providing the cross section data layerwise to the selective exposure means.

The following examples are intended to provide those of ordinary skill in the art with a complete disclosure and description of how to make and use the novel electrolyte compositions of the invention, and are not intended to limit the scope of

what the inventors regard as their invention in any way. Efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperatures, etc), but some experimental error and deviation should, of course, be allowed for. Unless indicated otherwise, parts are parts by weight, temperatures are in degrees centigrade, and pressure is at or near atmospheric. All chemicals, reagents, and the like, are commercially available or are otherwise readily synthesized using conventional techniques well known in the art.

Example 1

Silicon Nitride Slurry Preparation

The following components were weighed into a beaker: pentaerythritol triacrylate, 32.81 g (6.3 wt.%); 2-hydroxyethyl acrylate, 68.41 g (13.2 wt.%); and dibutylphthalate ("DBP") 50.53 g (9.7 wt.%). To this mix, Hypermer® KD-1 (6.615 g, 1.3 wt.%) and a visible photoinitiator (Spectra Group Limited, In., Maumee, OH) were added. The visible light photoinitiator has the following composition: H-Nu 470B (0.525 g); 4-octyloxyphenyl-phenyl iodonium (1.260 g); and N,N-dimethyl-2,6 diisopropylaniline (2.100 g). The mix was transferred into a ball mill for further mixing. Silicon nitride (NCZ-5102 (4% yttria silicon nitride), Saint-Gobain/Norton Industrial Ceramics Corporation, Northboro, MA) (357 g 68.7 wt.%) was added while mixing at a slow speed. After addition of the silicon nitride balls, the ball mill was run for about one hour. The slurry viscosity was determined using a Brookfield model DV-II+ viscometer to be 900 cps at a shear rate of 4 sec^{-1}.

Example 2

Multilayer Photopolymerization of a Silicon Nitride Slurry Using a DLP Projector

The silicon nitride slurry prepared as described in Example 1 is applied as 2 mil-thick layers on a build table, and each layer is photoexposed for about 50 seconds using a digital light processing projector (InFocus Systems Lite Pro 620).

Example 3

Multilayer Photopolymerization of a Silicon Nitride Slurry Using an LCD Projector

The silicon nitride slurry prepared as described in Example 1 is applied as 2 mil-thick layers on a build table, and each layer is photoexposed for about 50 seconds using an LCD projector (InFocus Systems Lite Pro 210).

Example 4

Multilayer Photopolymerization of a Silicon Nitride Slurry Using an Optical System for Laser Scanning

The silicon nitride slurry prepared as described in Example 1 is applied as 2 mil-thick layers on a build table, and each layer is photoexposed translating an optical system for laser scanning (Xerox Corp.) over the surface of the layers.

Example 5

Multilayer Photopolymerization of a Silicon Nitride Slurry Using an LCD Panel Mask

The silicon nitride slurry prepared as described in Example 1 was applied as 2-mil thick layers on a build table and each layer was photoexposed for about 50 seconds through an LCD panel using a 1000 W xenon lamp.

Example 6

Film Fabrication Prepared by Photocuring a Silicon Nitride Slurry

The following components were weighed into a beaker: pentaerythritol triacrylate, 16,569 g (3.2 wt.%); 2-hydroxyethyl acrylate, 98.59 g (18.5 wt.%); and 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 24.15 g (4.6 wt.%), DBP, 16.43 g (3.1 wt.%), Hypermer® KD-1, 6.226 g (1.2 wt.%), silicon nitride, 357 g (68 wt.%), a visible photoinitiator (Spectra Group Limited, In., Maumee, OH). The visible light photoinitiator has the following composition: H-Nu 470B (0.516 g); 4-octyloxyphenyl-phenyl iodonium (4.830 g); and N,N-dimethyl-2,6 diisopropylaniline (2.215 g). The mix was transferred into a ball mill for further mixing. The slurry viscosity was determined using a Brookfield model DV-II+ viscometer to be 1250 cps at a shear rate of 2 sec^{-1}.

The silicon nitride slurry was applied on a Kapton® film and photoexposed to a 300 W tungsten lamp. The slurry solidified in sixty seconds to yield a film 5.5 mil

thick. The thickness was measured after rinsing the film with acetone to remove an uncured material.

Example 7

Silicon Nitride Slurry Preparation

The following components were weighed into a beaker: pentaerythritol triacrylate, 33.08 g (6.3 wt.%); 2-hydroxyethylacrylate, 68.25 g (13.0 wt.%); DBP, 50.4 g (9.6 wt.%); Hypermer® KD-1, 10.50 g (2 wt.%); the visible photoinitiator composition described in Example 6, 3.885 g (0.74 wt.%); and alumina, 358.89 g (68.36 wt.%). The slurry was applied on a Kapton® film and photocured by exposure to a tungsten lamp as described in Example 6. A 6 mil-thick film was formed after a 30-second exposure.

Example 8

Polymer Multilayer Fabrication

A mix of pentaerythritol triacrylate, 16.54 g (33.1 wt.%); 2-hydroxyethylacrylate, 33.1 g (66.2 wt.%); and the photoinitiator composition described in Example 6 was prepared. The mix is applied in 2 mil-thick layers on a build table and each layer is photoexposed for about 30 seconds using a digital light processing ("DLP") processing projector (InFocus Lite Pro 620).

We claim:

1. A method for fabricating a three-dimensional object, comprising:

(a) applying a first layer of a photocurable composition on a build table, wherein the layer is sufficiently thin to permit photopolymerization substantially the entirety thereof;

(b) exposing the first layer to actinic radiation using a selective photopolymerization means for a period of time sufficient to photopolymerize an area of the layer corresponding to a cross section of the object,

wherein the selective photoexposure means comprises (i) a digital light processing ("DLP") projector, (ii) a liquid crystal display ("LCD") projector, (iii) an optical system for laser scanning, or (iv) a source of actinic radiation and an LCD panel displaying a computer-generated electronic mask; and

(c) repeating steps (a) and (b), so as to apply additional layers of the composition to the previously photopolymerized layer, wherein after application of each additional layer the selective photopolymerization means is changed to correspond to a cross section of the object immediately adjacent to the cross section of the previously prepared layer, until fabrication is complete.

2. The method of claim 1, wherein the photocurable composition comprises a plasticizing solvent, a surfactant, a polymerizable monomer or oligomer, and, optionally, a ceramic powder, a metallic powder, a wax, or a mixture thereof.

3. The method of claim 2, wherein the composition comprises a ceramic powder.

4. The method of claim 3, wherein the ceramic powder is selected from the group consisting of silica, silicon nitride, silicon carbide, boron carbide, titanium carbide, titanium nitride, tungsten carbide, molybdenum oxide, alumina, zirconia, silicon, ferrite, and mixtures thereof.

5. The method of claim 3, wherein the composition comprises a metallic powder.

6. The method of claim 6, wherein the metallic powder is selected from the group consisting of aluminum, copper, nickel, iron, magnesium, silicon, titanium, tungsten, and mixtures and alloys thereof.

7. The method of claim 3, wherein the composition comprises a wax.

8. The method of claim 1, wherein the actinic radiation is near infrared light or visible light.

9. An apparatus for automated layer-by-layer fabrication of a three-dimensional object from a computer model, comprising:

(a) a build table on which the three-dimensional object is fabricated;

(b) means for depositing a predetermined quantity of a photopolymermizable composition onto the work surface;

(c) means for leveling the deposited composition to a layer having a predetermined thickness;

(d) means for selective photoexposure of the photopolymerizable composition comprising (i) a digital light processing ("DLP") projector, (ii) a liquid crystal display ("LCD") projector, (iii) an optical system for laser scanning, or (iv) a source of actinic radiation and an LCD panel displaying a computer-generated electronic mask;

(e) a computer-aided design/computer-aided manufacturing (CAD/CAM) system comprising a means for generating a three-dimensional computer model representation of the object, a means for slicing the representation into a plurality of successive layers having predetermined thickness, a means for producing cross section data of the layers of the object, and a means for providing the cross section data layerwise to the means for selective photoexposure of the photopolymerizable composition.

10. The apparatus of claim 9, wherein the means for selective photoexposure comprises a DLP projector.

11. The apparatus of claim 9, wherein the means for selective photoexposure comprises an optical system for laser scanning.

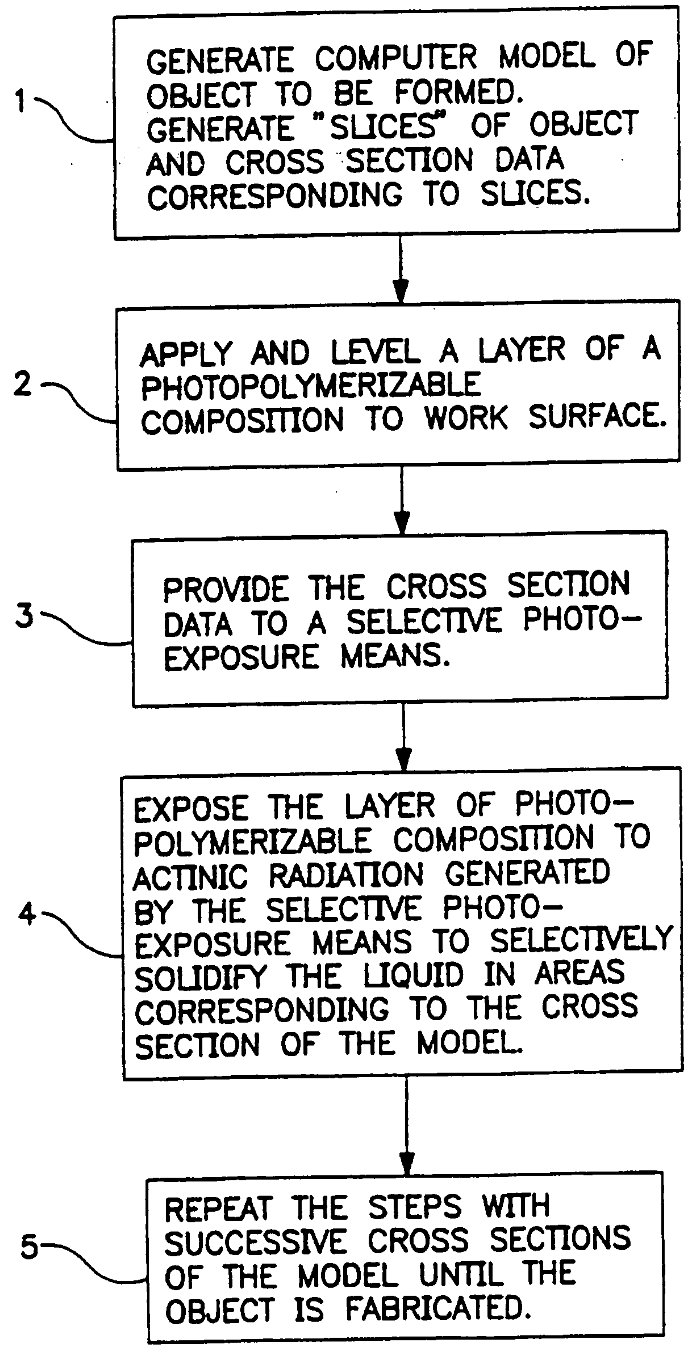
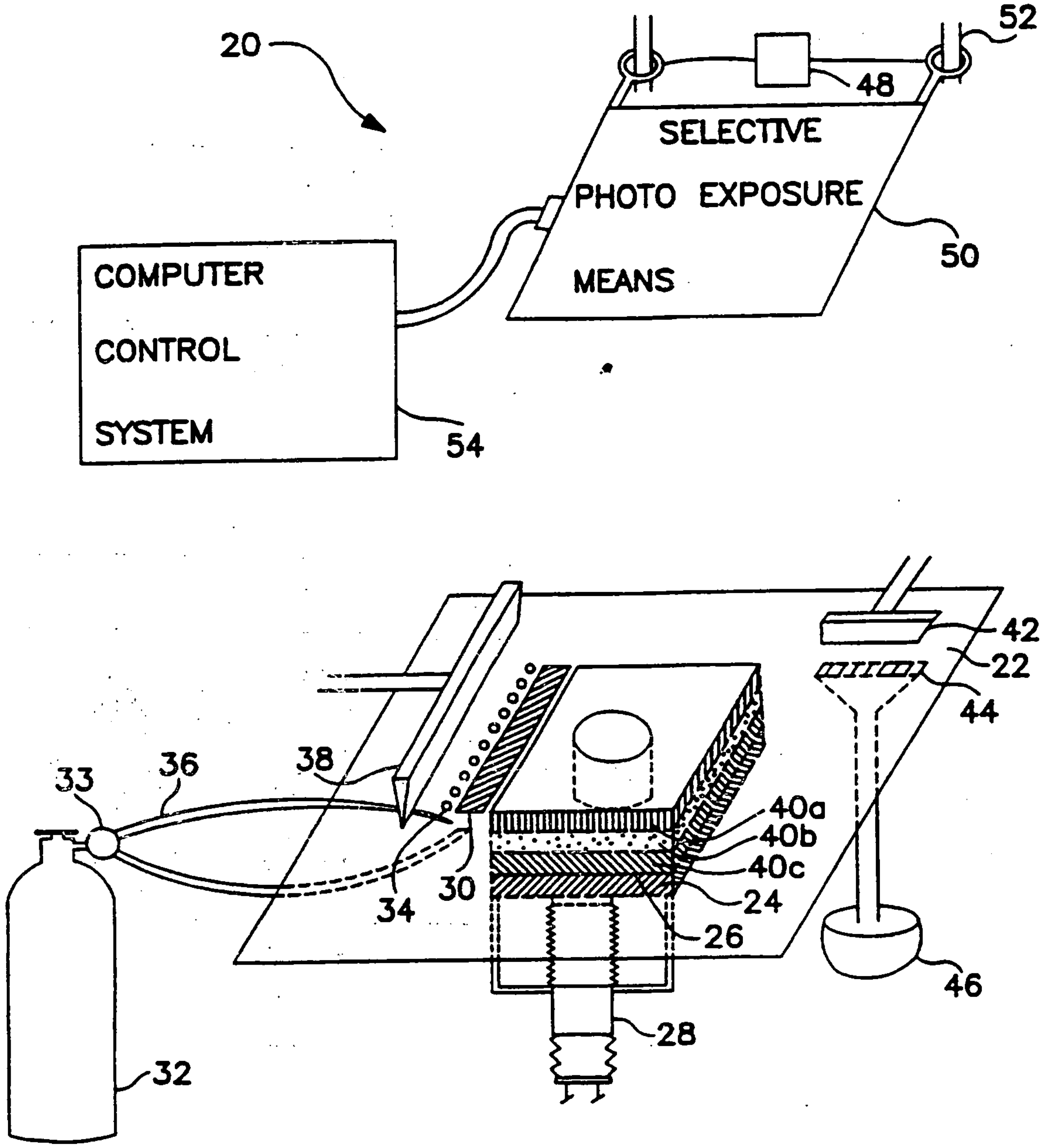

1
GENERATE COMPUTER MODEL OF OBJECT TO BE FORMED. GENERATE "SLICES" OF OBJECT AND CROSS SECTION DATA CORRESPONDING TO SLICES.
2
APPLY AND LEVEL A LAYER OF A PHOTOPOLYMERIZABLE COMPOSITION TO WORK SURFACE.
3
PROVIDE THE CROSS SECTION DATA TO A SELECTIVE PHOTO-EXPOSURE MEANS.
4
EXPOSE THE LAYER OF PHOTO-POLYMERIZABLE COMPOSITION TO ACTINIC RADIATION GENERATED BY THE SELECTIVE PHOTO-EXPOSURE MEANS TO SELECTIVELY SOLIDIFY THE LIQUID IN AREAS CORRESPONDING TO THE CROSS SECTION OF THE MODEL.
5
REPEAT THE STEPS WITH SUCCESSIVE CROSS SECTIONS OF THE MODEL UNTIL THE OBJECT IS FABRICATED.

FIG. 1


20
52
48
SELECTIVE
PHOTO EXPOSURE
MEANS
50
COMPUTER
CONTROL
SYSTEM
54
42
22
44
38
36
33
40a
40b
40c
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26
30
34
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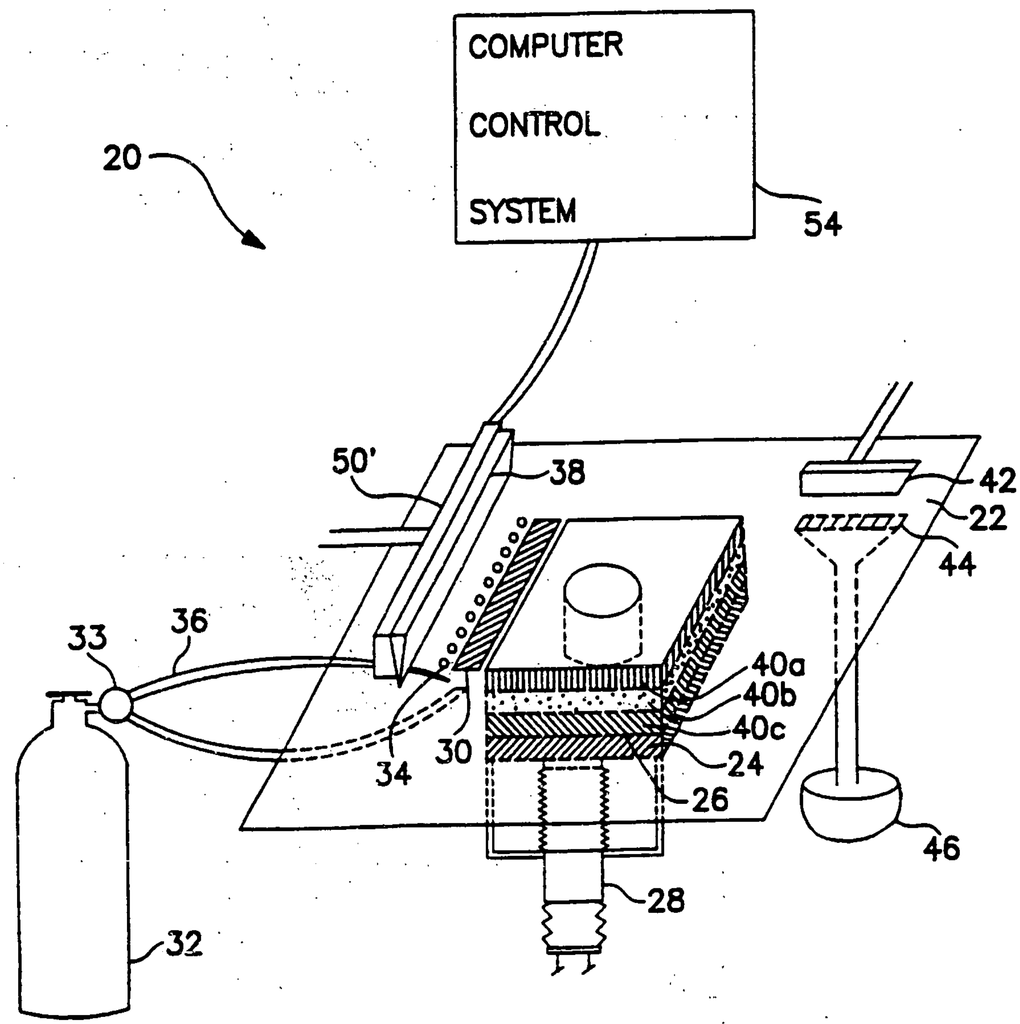
FIG. 2


COMPUTER
CONTROL
SYSTEM
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50'
38
42
22
44
36
33
40a
40b
40c
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FIG. 3

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 97/13050

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C67/00 G02F1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 5 026 146 A (HUG WILLIAM F ET AL) 25 June 1991 see the whole document	1,9,11 2-4,8,10
Y	EP 0 393 673 A (DU PONT) 24 October 1990 see claims	2-4,8
P,Y	WO 97 19435 A (OPDENBERG RONALD EVERT) 29 May 1997 see the whole document	10
X Y	PATENT ABSTRACTS OF JAPAN vol. 096, no. 010, 31 October 1996 & JP 08 142203 A (JAPAN SYNTHETIC RUBBER CO LTD), 4 June 1996, see abstract; figures 1-8	1,9 2-6,10

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
18 November 1997	28/11/1997

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Mathey, X

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No.
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X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 023 (M-920), 17 January 1990 & JP 01 263031 A (NEC CORP), 19 October 1989, see abstract; figures 1-4	1,9

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

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